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## U.S. PATENT DOCUMENTS

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### (54) Coloring composition and inkjet recording method

(57) The invention provides a water-soluble ink capable of forming an image having good color hue and high fastness in various use and environmental conditions, which comprises a coloring composition comprising a disazo dye represented by the following formula 1:  $A_1-N=N-A_2-N=N-A_3$  and at least one other dye having

a specific structure; in formula 1,  $A_1$ ,  $A_2$  and  $A_3$  each independently represents an aromatic group which may be substituted or a heterocyclic group which may be substituted, and  $A_1$  and  $A_3$  each is a monovalent group and  $A_2$  is a divalent group.

**Description****FIELD OF THE INVENTION**

5 [0001] The present invention relates to a coloring composition (preferably a coloring composition (an ink composition, preferably an inkjet ink composition) for forming a color image) containing a combination of an azo dye mainly using a heterocyclic ring as the raw material with an azo dye or the like having a specific structure, and at least a solvent. The present invention also relates to an inkjet recording method using the coloring composition (preferably, black coloring composition).

**BACKGROUND OF THE INVENTION**

10 [0002] The inkjet recording method is abruptly overspread and still making a progress, because the material cost is low, high-speed recording can be performed, noises are less generated at the recording and color recording is facilitated.

15 [0003] The inkjet recording method includes a continuous system of continuously jetting out a liquid droplet and an on-demand system of jetting out a liquid droplet according to image information signals, and the ejection system therefor includes a system of jetting out a liquid droplet by applying a pressure using a piezoelectric element, a system of jetting out a liquid droplet by generating bubbles in an ink under heat, a system using an ultrasonic wave, and a system of jetting out a liquid droplet by suction using an electrostatic force. With respect to the inkjet recording ink, an aqueous ink, an oily ink or a solid (fusion-type) ink is used.

20 [0004] The coloring agent used in such an inkjet recording ink is required to exhibit good solubility or dispersibility in a solvent, enable high-density recording, provide good color, be fast to light, heat and active gases in the environment (for example, oxidative gas (e.g., NO<sub>x</sub>, ozone) and SO<sub>x</sub>) and highly resistant against water and chemicals, ensure good fixing property and less blurring on an image-receiving material, give an ink having excellent storability, have high purity and no toxicity and be available at a low cost. However, it is very difficult to find out a coloring agent satisfying these requirements in a high level. In particular, a dye having good color hue and being fast to light, humidity and heat, especially at the printing on an image-receiving material having an ink-accepting layer containing a porous inorganic white pigment particle, being fast to oxidative gases in the environment, such as ozone, is strongly demanded.

25 [0005] As the dye for black color, a mixture of a disazo or trisazo dye with a yellow or magenta dye has been heretofore developed and for the raw material of these disazo and trisazo dyes, non-heterocyclic compounds such as phenol, naphthol, naphthylamine and aniline are being widely used. As for the disazo dye obtained from such raw materials, the dyes disclosed, for example, in European Patent No. 0761771 and Japanese Patent No. 2716541 are known, however, these dyes all are poor in the light fastness and furthermore, the fastness to oxidative gases such as ozone is extremely insufficient. Therefore, if such a dye is mixed with a yellow or magenta dye, the problem of poor light fastness or very insufficient fastness to oxidative gases such as ozone remains unsolved.

**SUMMARY OF THE INVENTION**

30 [0006] The present invention has been made to solve those problems in conventional techniques and achieve the following objects.

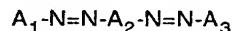
[0007] That is, an object of the present invention is to provide an ink composition for printing such as inkjet printing or an aqueous ink composition for writing, which gives a color image or colored material having good black color hue and excellent fastness.

35 [0008] Another object of the present invention is to provide an ink composition for inkjet recording and an inkjet recording method, which can form an image having good black color hue and high fastness to light and active gases in the environment, particularly ozone gas.

[0009] As a result of extensive investigations on various dye compound derivatives to obtain a dye ensuring good color hue and high fastness to light and ozone, the present inventors have found that the above-described objects of the present invention can be attained by mixing an azo dye mainly using a heterocyclic ring as the raw material with an azo dye having a specific structure and/or a metal phthalocyanine dye.

55 1. A coloring composition comprising a dye represented by the following formula 1 and at least one dye selected from the dyes represented by the following formulae 2 to 6:

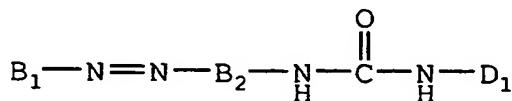
Formula 1:



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Formula 2:

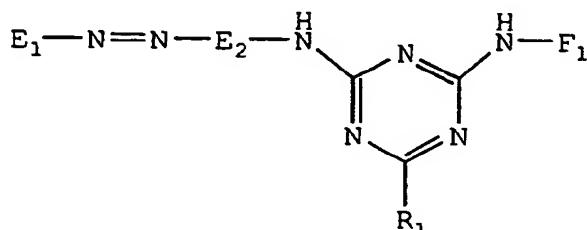
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Formula 3:

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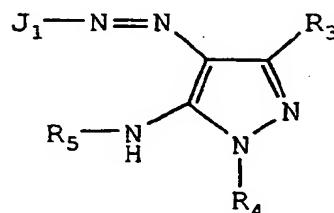
Formula 4:



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Formula 5:

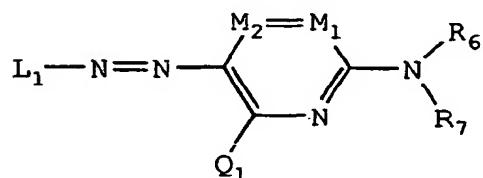
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Formula 6:

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wherein in formula 1,  $A_1$ ,  $A_2$  and  $A_3$  each independently represents an aromatic group which may be substituted, or a heterocyclic group which may be substituted, and  $A_1$  and  $A_3$  each is a monovalent group and  $A_2$  is a divalent group;

55

in formula 2,  $B_1$  and  $B_2$  each independently represents an aromatic group which may be substituted, or a heterocyclic group which may be substituted, and  $D_1$  represents an arbitrary substituent;

in formula 3,  $E_1$  and  $E_2$  each independently represents an aromatic group which may be substituted or a hetero-

cyclic group which may be substituted,  $E_1$  is a monovalent group and  $E_2$  is a divalent group,  $F_1$  represents an arbitrary substituent, and  $R_1$  represents a monovalent group;

in formula 4,  $G_1$  and  $G_2$  each independently represents an aromatic group which may be substituted, or a heterocyclic group which may be substituted, and  $R_2$  represents an arbitrary substituent except for hydrogen;

in formula 5,  $R_3$  and  $R_5$  each independently represents a hydrogen atom, an alkyl group, a cycloalkyl group, an aralkyl group, an alkoxy group or an aryl group,  $R_4$  represents a hydrogen atom, an alkyl group, a cycloalkyl group, an aralkyl group, a carbamoyl group, an acyl group, an aryl group or a heterocyclic group, and  $J_1$  represents an aromatic group which may be substituted, or a heterocyclic group which may be substituted; and

in formula 6,  $L_1$  represents an aromatic group which may be substituted, or a heterocyclic group which may be substituted;  $M_1$  and  $M_2$  each represents  $=CR_8-$  or  $-CR_9=$ , or either one of  $M_1$  and  $M_2$  represents a nitrogen atom and the other represents  $=CR_8-$  or  $-CR_9=$ ;  $R_6$  and  $R_7$  each independently represents a hydrogen atom, an aliphatic group, an aromatic group, a heterocyclic group, an acyl group, an alkoxy carbonyl group, an aryloxy carbonyl group, a carbamoyl group, an alkylsulfonyl group, an arylsulfonyl group or a sulfamoyl group, and each group may further have a substituent;  $Q_1$ ,  $R_8$  and  $R_9$  each independently represents a hydrogen atom, a halogen atom, an aliphatic group, an aromatic group, a heterocyclic group, a cyano group, a carboxyl group, a carbamoyl group, an alkoxy carbonyl group, an aryloxy carbonyl group, a heterocyclic oxy carbonyl group, an acyl group, a hydroxy group, an alkoxy group, an aryloxy group, a heterocyclic oxy group, a silyloxy group, an acyloxy group, a carbamoyloxy group, an alkoxy carbonyloxy group, an aryloxy carbonyloxy group, an amino group, an acylamino group, a ureido group, a sulfamoyl amino group, an alkoxy carbonyl amino group, an aryloxy carbonyl amino group, an alkylsulfonyl amino group, an arylsulfonyl amino group, a heterocyclic sulfonyl amino group, a nitro group, an alkylthio group, an arylthio group, an alkylsulfonyl group, an arylsulfonyl group, a heterocyclic sulfonyl group, an alkylsulfinyl group, an arylsulfinyl group, a heterocyclic sulfinyl group, a sulfamoyl group, a sulfo group or a heterocyclic thio group, and each group may be further substituted; and  $R_8$  and  $R_6$ , or  $R_6$  and  $R_7$  may combine to form a 5- or 6-membered ring.

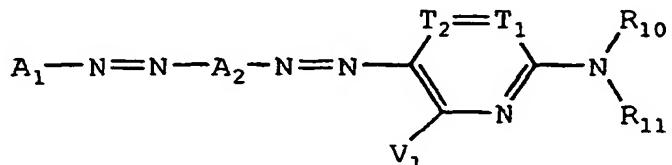
2. The coloring composition as described in the item 1, wherein A<sub>3</sub> in formula 1 represents an aromatic heterocyclic group.

3. The coloring composition as described in the item 1 or 2, wherein at least one of  $A_1$  and  $A_2$  in formula 1 represents an aromatic heterocyclic group.

4. The coloring composition as described in any one of the items 1 to 3, wherein  $A_3$  in formula 1 represents an aromatic nitrogen-containing 6-membered heterocyclic group.

5. The coloring composition as described in any one of the items 1 to 4, wherein the dye represented by formula 1 is a dye represented by the following formula 7:

### Formula 7:

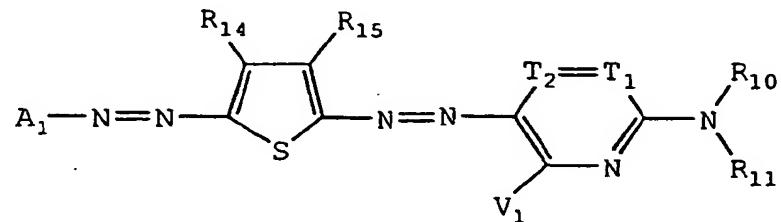


wherein  $T_1$  and  $T_2$  each represents  $=CR_{12}-$  or  $-CR_{13}=$ , or either one of  $T_1$  and  $T_2$  represents a nitrogen atom and the other represents  $=CR_{12}-$  or  $-CR_{13}=$ ;  $V_1$ ,  $R_{12}$  and  $R_{13}$  each independently represents a hydrogen atom, a halogen atom, an aliphatic group, an aromatic group, a heterocyclic group, a cyano group, a carboxyl group, a carbamoyl group, an alkoxy carbonyl group, an aryloxycarbonyl group, a heterocyclic oxycarbonyl group, an acyl group, a hydroxy group, an alkoxy group, an aryloxy group, a heterocyclic oxy group, a silyloxy group, an acyloxy group, a carbamoyloxy group, an alkoxy carbonyloxy group, an aryloxycarbonyloxy group, an amino group (including an alkylamino group, an arylamino group and a heterocyclic amino group), an acylamino group, a ureido group, a sulfamoylamino group, an alkoxy carbonylamino group, an aryloxycarbonylamino group, an alkylsulfonylamino

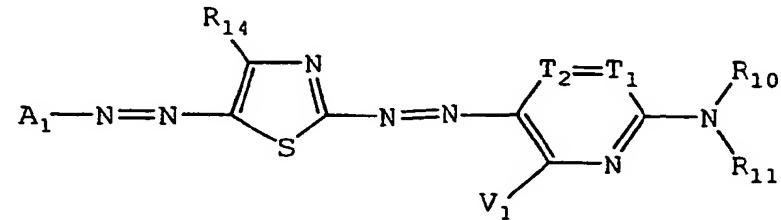
group, an arylsulfonylamino group, a heterocyclic sulfonylamino group, a nitro group, an alkylthio group, an arylthio group, a heterocyclic thio group, an alkylsulfonyl group, an arylsulfonyl group, a heterocyclic sulfonyl group, an alkylsulfinyl group, an arylsulfinyl group, a heterocyclic sulfinyl group, a sulfamoyl group or a sulfo group, and each group may be further substituted;  $R_{10}$  and  $R_{11}$  each independently represents a hydrogen atom, an aliphatic group, an aromatic group, a heterocyclic group, an acyl group, an alkoxy carbonyl group, an aryloxycarbonyl group, a carbamoyl group, an alkylsulfonyl group, an arylsulfonyl group or a sulfamoyl group, and each group may further have a substituent, provided that  $R_{10}$  and  $R_{11}$  do not represent a hydrogen atom at the same time; and  $R_{12}$  and  $R_{13}$ , or  $R_{10}$  and  $R_{11}$  may combine to form a 5- or 6-membered ring.

10 6. The coloring composition as described in the item 5, wherein the dye represented by formula 7 is a dye represented by the following formula 8 or formula 8-2:

15 Formula 8:



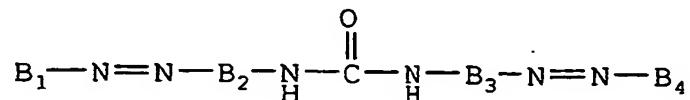
25 Formula 8-2:



35 wherein  $R_{14}$  and  $R_{15}$  each has the same meaning as  $R_{12}$  of formula 7 and  $A_1$ ,  $R_{10}$ ,  $R_{11}$ ,  $T_1$ ,  $T_2$  and  $V_1$  have the same meanings as in formula 7.

40 7. The coloring composition as described in any one of the items 1 to 6, wherein the dye represented by formula 2 is a dye represented by the following formula 9:

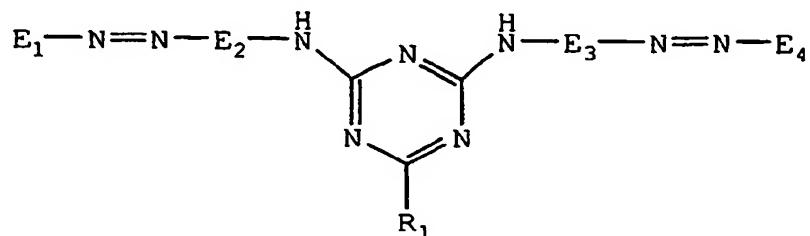
45 Formula 9:



50 wherein  $B_1$ ,  $B_2$ ,  $B_3$  and  $B_4$  each independently represents an aromatic group which may be substituted, or a heterocyclic group which may be substituted.

55 8. The coloring composition as described in any one of the items 1 to 7, wherein the dye represented by formula 3 is a dye represented by the following formula 10:

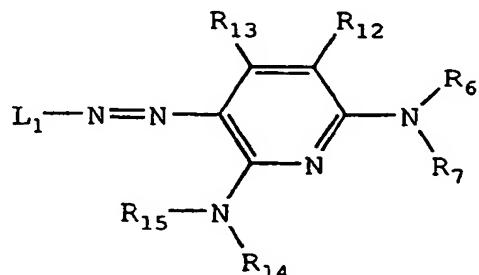
### Formula 10:



wherein  $E_1$ ,  $E_2$ ,  $E_3$  and  $E_4$  each independently represents an aromatic group which may be substituted, or a heterocyclic group which may be substituted, and  $R_1$  represents a monovalent substituent.

9. The coloring composition as described in any one of the items 1 to 8, wherein the dye represented by formula 6 is a dye represented by the following formula 11:

Formula 11:



wherein  $L_1$ ,  $R_6$  and  $R_7$  have the same meanings as in formula 6,  $R_{12}$  and  $R_{13}$  have the same meanings as  $R_8$  and  $R_9$ , respectively,  $R_{14}$  and  $R_{15}$  each independently represents a hydrogen atom, an aliphatic group, an aromatic group, a heterocyclic group, an acyl group, an alkoxy carbonyl group, an aryloxy carbonyl group, a carbamoyl group, a sulfonyl group or a sulfamoyl group.

10. The coloring composition as described in any one of the items 1 to 9, which further comprises a metal phthalocyanine dye.

11. The coloring composition as described in the item 10, wherein the metal phthalocyanine dye is a dye represented by the following formula 12: